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(54) **Title**
MODIFIERS FOR CEMENTITIOUS MATERIALS

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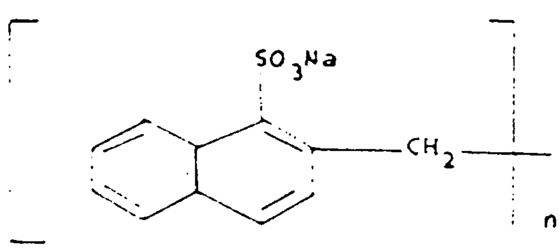
(56) **Prior Art Documents**
58804/80 537598 C04B 13/28
53192/73 458177 18.5, 18.3
US 3465825

(57) **Claim**

1. A modifier for cementitious mortars and the like comprising:-

70-30 parts by weight of hydroxy propyl methyl cellulose,

10-40 parts by weight of a sodium salt of a naphthalene formaldehyde sulphonate having the general formula:



wherein n is from 2-10;

and a substantially chlorine free, non-efflorescing cement accelerator.

6. A modified cement mortar having the composition:- 1 part by volume of portland cement, 3-6 parts by volume of sand, and 0 001-0.010 parts by volume of a modifier as defined in any one of claims 1-5.

7. A method of modifying a cementitious mortar or the like comprising mixing together the dry mortar ingredients with 0.001-0.010 parts by weight of a dry powdered modifier according to any one of claims 1-5 and subsequently adding water to a desired consistency.

AUSTRALIAN PATENT OFFICE

COMMONWEALTH OF AUSTRALIA

The Patents Act 1952-1973

AMENDED

APPLICATION FOR A PATENT

572111

~~I~~ We, A.V. SYNTEC PTY. LTD.

of 27 Edgar Street, Northgate, 4013, Queensland, Australia

hereby apply for the grant of a Patent for an invention entitled:

MODIFIERS FOR CEMENTITIOUS MATERIALS

which is described in the accompanying Provisional/~~Complete~~ Specification.

~~My~~ Our address for service is: C/- G.R. Cullen & Company. Patent Attorneys. of Medibank Building, 82 Ann Street, Brisbane, in the state of Queensland, Commonwealth of Australia.

DATED this Third day of May 1985

... AND AMENDMENTS

... 7 . 3 . 88

A.V. SYNTEC PTY. LTD.
By its Patent Attorneys
G.R. CULLEN & COMPANY.

Peter C. Fisher.

To:

The Commissioner of Patents,
Commonwealth of Australia.

COMMONWEALTH OF AUSTRALIA
THE PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention entitled:

Insert Title of Invention

"MODIFIERS FOR CEMENTITIOUS MATERIAL"

Insert Full Name(s) and Address(es)

I/~~We~~ Michael John MARTIN

of 2 Neulands Road, INDOOROOPILLY, 4068, Brisbane, Queensland, Australia,

do solemnly and sincerely declare as follows:–

Insert Full Name(s) of Applicant(s)

~~1. I am/We are the applicant(s) for the patent~~ -

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorised by SYNTEC CHEMICALS PTY. LTD.

the applicant(~~s~~) for the patent to make this declaration on its ~~their~~ behalf.

2. I am/~~We are~~ the actual inventor(~~s~~) of the invention ~~referred to in the basic application(s)~~

~~(or, where a person other than the inventor is the applicant)~~

Full Name(s) and Address(es) of Inventor(s)

~~2.~~

State how Applicant(s) derive title from inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s)

~~is/are the actual inventor(s) of the invention~~ and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:–

The said Applicant, Syntec Chemicals Pty. Ltd. is the Assignee of the said invention from the said actual Inventor, Michael John Martin.

*Note: Paragraphs 3 and 4 need only be completed for a Convention Application

Basic Country(ies)
Priority Date(s)
Basic Applicant(s)

~~3. The basic application(s) as defined by Section 141 of the Act was/were made~~

in .... on ....
by ....
in .... on ....
by ....

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the ~~first~~ application(s) made in a Convention country in respect of the invention(s) ~~the subject of the application~~.

Declared at Brisbane this 6th day of [illegible] 1984

To: The Commissioner of Patents

[signature]

Signature of Declarant(s)
M.J. Martin, DIRECTOR

G. R. CULLEN & COMPANY

572111

33766/84

COMMONWEALTH OF AUSTRALIA

The Patents Act 1952-1969

Name of Applicant: SYNTEC ~~CHEMICALS~~ PTY. LTD.

Address of Applicant: 27 [illegible] Street, [illegible]GATE, 4[illegible], Queensland, Australia

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COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"MODIFIERS FOR CEMENTITIOUS MATERIAL"

The following statement is a full description of the invention including the best method of performing it known to us:

This invention is concerned with [illegible] for cementitious materials such as [illegible] to improve certain properties thereof.

The invention is concerned particularly, [illegible] not exclusively, with modifiers for [illegible] workability and strength characteristics.

Most cement mortars used for [illegible] or concrete blocks comprise 1 part by [illegible]

1 part by [illegible]

5-6 parts by [illegible]

High strength mortars ideally have only sufficient water added to the mix to hydrate the cement as excess water present during hydration substantially [illegible] the ultimate properties of the cured mortar. A [illegible] difficulty of an "ideal" mortar containing an optimum water content is that the mortar rapidly becomes stiff and loses its "workability" as the cement hydrates. Addition by bricklayers of extra water to soften the mix at this stage is often the cause of poor mortar performance particularly in relation to compressive strength and [illegible] strength of the cured mortar.

"Workability" of a cement mortar is a [illegible] of characteristics which relate to the degree of fluidity of the wet mortar mix. A workable mortar has early fluidity enabling ease of application to a course of bricks or blocks and ease of bedding of a fresh brick or block. At the same time a workable mortar should lose its initial fluidity and stiffen at a relatively short interval to provide adequate support beneath a previously laid course. Initial workability of a fresh mortar mix is assessed by traditional means such as a slump test or flow and water retention tests set forth in Australian Standard No. AS1316 "Masonry Cement".

The workability of a mortar mix can be affected seriously by high ambient temperature [illegible] which

increase moisture evaporation and cement hydration.

Another very important factor is the nature of the brick or block itself which can affect the workability of the mortar. Often this can have a seriously detrimental effect on the bond between the mortar and the brick or block. Accordingly, it is a requirement of the mortar to compensate for many variables including ambient temperature conditions as well as the properties of the brick or block in order to ensure optimum performance.

Although the requirements for cement mortars for brickwork and blockwork are set out in the Appendices to Australian Standards AS 1640 and AS 1475 respectively, in practice most bricklayers tend to mix and use mortars according to their own requirements rather than undergo any inconvenience which may interfere with their laying rate. The result of this is that considerable inconsistency in mortar bond strengths will occur from batch to batch.

Of all the properties required of a good mortar mix, water retention is the most important as it is this property which has the most profound effect on bond strength.

"Water retention" is a standard measure of the property which enables a mortar to resist the "suction" exerted by a porous brick or block. Good water retention properties are important for three reasons: first, because water is prevented from bleeding out of the mortar; secondly, because the mortar bed is prevented from stiffening too much before the brick can be placed in position; and thirdly, because sufficient water is retained in the mortar to ensure proper hydration of the cement.

The SAA Codes for brickwork and blockwork both require a water retention value of at least 70% when tested in accordance with the method set forth in AS 1316. Briefly, the test involves a determination of mortar flow before and after applying "suction" to the mortar for one

minute.

$$\text{Water Retention (\%)} = \frac{\text{Flow after suction}}{\text{Flow before suction}} \times 100$$

The strength of the bond [illegible] between the brick and mortar depends inter alia, on the [illegible] achieved between the absorption characteristics of the brick on the one hand and the water retention [illegible] of the mortar on the other.

For example, when bricks with weak absorption [illegible] combined with mortar with strong water retention, the bricks will "float" on the mortar bed. The effects of such a combination are that the mortar takes too long to stiffen or cure delaying construction and [illegible] at the interface with the result that the bond is poor.

If bricks with strong absorption are combined with mortar having poor water retention, the opposite effect will be observed. The mortar stiffens too rapidly and the next course of bricks cannot be bedded properly. Further, the bricks may absorb sufficient water from the mortar that there is insufficient left to properly hydrate the cement. In any event, the bond is poor.

The standard measure of a brick's absorption characteristics, so far as they affect bond, is the initial rate of absorption (IRA). The IRA is the amount of water absorbed by a standard area of the bed face of the brick in one minute and is the property hitherto referred to as "suction".

Clay bricks, depending on the nature of the clay and the method of production are generally classified into three groups having high, intermediate and low IRA's. Generally speaking, clay bricks have an IRA in the range 0.2 - 6.5 kg $m^{-2}min^{-1}$ whereas concrete bricks and blocks have an IRA in the range 0.7 - 1.5. The IRA of a brick or block will of course vary depending on the moisture content at the time of testing.

Thus it can be seen that there are many variables

to be taken into account in mixing of mortars for a particular brick or block laying operation. Many of these variables give rise to contradictory requirements.

In an endeavour to provide high quality mortars with consistent properties it is possible to chemically modify the mortar.

Workability problems in the use of mortar mixes may be overcome to some degree by the use of certain additives which may be broadly categorized into:

i) water retaining agents

ii) water reducing agents

iii) accelerators

iv) retardants.

The most commonly used water retaining agent is a carboxy methyl cellulose (CMC) which finds its major application in cement mortars applied to bricks or blocks with a high rate of initial absorption such as Calcium Silicate bricks. CMC is difficult to dissolve in water at ambient temperatures and may give rise to an uncontrolled stiffening of the mortar during mixing. When mixed with a cement mortar, conventional CMC additives are inclined to create an early stiffening of the mortar although if sufficient shear is applied to the mix a certain thixotropy may be noted. In general, the early stiffening is disadvantageous and thus a retardant must be used to maintain workability. Of more recent times, a delayed solubility CMC has been used to avoid early stiffening but this does not overcome the problems of poor workability, particularly at low ambient temperatures.

Water reducing agents enable a reduction in the water/cement ratio at a given workability compared with an unmodified mortar and these are generally known as plasticizers.

Where a high rate of initial absorption is not a controlling factor, a plasticizer may be added to the mortar

mix to increase the degree of fluidity thereof without the necessity of additional water.

The most commonly used plasticizers have specific functions and are chosen in accordance with the strength requirements of the cured mortar or more frequently the conditions under which the mortar is to be used. Plasticizers may be categorized as,

A. Normal water reducing agents,

B. Accelerating water reducing mixtures which accelerate cement hydration under ambient conditions.

C. Retarding water reducing mixtures which retard cement hydration under ambient conditions.

D. Air entraining agents which entrain microscopic air bubbles to reduce mortar viscosity, and

E. Superplasticizers which enable massive additions thereof without the deleterious effects normally associated with excess concentrations of types A, B or C above.

When adding workability modifiers to batches of mortar, most laborers tend to guess the quantity required and tend to "overdose" the batch. Excess concentrations of additives A-D will almost invariably reduce mortar quality.

The most widely used modifier in cement mortars is hydrated lime which extends mortar workability by its retardant effect. In addition, bricklayers prefer to use "bricklayers sand" instead of washed, sharp beach or river sand recommended for its superior strength qualities. "Bricklayers sand" contains a certain amount of clay or other micro-fine impurities which improve the workability of a mortar mix but is known to have deleterious effects on the mechanical properties and bond strength of a cured mortar. Hydrated lime is relatively expensive and has the serious disadvantage of contributing to unsightly efflorescence of calcium salts on finished clay brick or

concrete block masonry.

Typical water reducing agents are exemplified as follows:

Normal	Purified lignosulphonate, lignosulphonate + air-detraining agent, hydroxy-carboxylic acid at low dosage, hydroxylated polymer at low dosage.
Accelerating	Lignosulphonate + $CaCl_2$, lignosulphonate + triethanolamine, lignosulphonate + Ca formate, hydroxy-carboxylic acid + $CaCl_2$.
Retarding	High sugar lignosulphonate, hydroxy-carboxylic acid, hydroxylated polymer.
Air-Entraining	Impure lignosulphonate, lignosulphonate + surfactant, hydroxy-carboxylic acid + surfactant.
Superplasticizers	Pure lignosulphonate, salt of formaldehyde-naphthalene sulphonate, salt of formaldehyde-melamine sulphonate.

Of these compositions, all, with the exception of certain naphthalene formaldehyde sulphonates possess one or more serious disadvantages in additives in cement mortars. These disadvantages include high cost, variable quality and/or undesirable accelerating, retarding or air entrainment properties which require addition of further modifiers to control ultimate cured mortar properties.

The composition and mechanism of accelerators and retardants is well known in the cement and concrete art and thus will be dealt with only briefly in this document.

Accelerators are usually chosen from calcium chloride, calcium formate and triethanolamine and are used to accelerate hydration of cement, often in conjunction with a plasticizer having retardant properties. Of these accelerators, calcium formate is the only readily water soluble, dry powder with stable storage properties.

Calcium formate, unlike other accelerators does not contribute to corrosion of reinforcing steels or cause efflorescence.

Most of the plasticizers when used alone in cement mortars act as retardants although polysaccharide polymers may be used for this purpose.

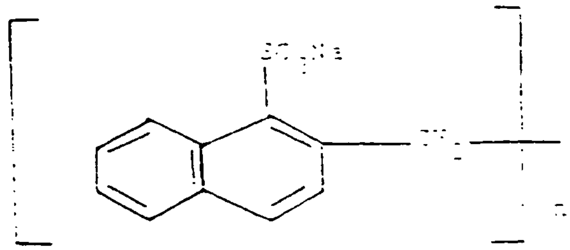
From the foregoing comments it will be clear that it is virtually impossible for the average bricklayer to modify the workability of an 'optimum' cement mortar without incurring some deleterious side effect in the cured mortar properties.

It is an aim of the present invention to overcome or alleviate the problems of prior art workability modifiers for concrete and cementitious mortars and at the same time provide enhanced physical and mechanical properties in the cured concrete and cementitious mortars.

According to one aspect of the present invention there is provided a modifier for cementitious materials comprising:-

70-30 parts by weight of hydroxy propyl methyl cellulose,

10-40 parts by weight of a sodium salt of a naphthalene formaldehyde sulphonate having the general formula:



wherein n is from 1-10;

and a substantially chlorine free, non-efflorescing cement accelerator.

Preferably said hydroxy propyl methyl cellulose has

a molecular weight of from 60,000 - 120,000.

Preferably said modifier comprises a dry powder readily soluble in water at ambient temperatures.

According to another aspect of the present invention there is provided a modified cement mortar having the composition:-

1 part by volume of portland cement

3-6 parts by volume of sand and

0.001-0.010 parts by volume of a modifier as described above.

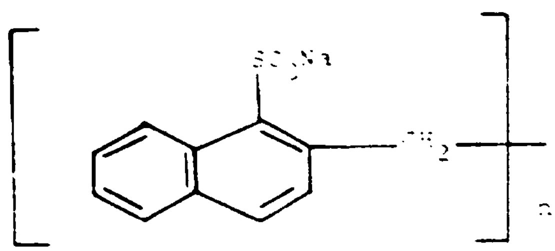
A preferred embodiment of the invention will now be described with reference to the following examples.

EXAMPLE 1 Modifier

The modifier preferably comprises a dry powder having the following composition:-

(a) 66.6 parts by weight of hydroxy propyl methyl cellulose having a molecular weight in the range 85,000 - 95,000;

(b) 26.74 parts by weight of a sodium salt of naphthalene formaldehyde sulphonate of the general formula:



wherein n is 7-10.

(c) 6.66 parts by weight of calcium formate.

Each of the dry powder ingredients is mixed together in the above proportions in any suitable powder mixer e.g., a ribbon blender, drum tumbler, high speed blade mixer etc. in either a batch or continuous manner. The dry powder mixture is then packed into suitable containers for storage, shipping and or dispensing. Most suitably the powder

mixture is packed into dispensers adapted to [illegible] the portions of predetermined quantities.

EXAMPLE 2 Mortar

A mortar comprising 1 part by volume of portland cement and 5 parts by volume of clean washed sharp sand was mixed in a cement mixer. 0.003 parts by volume of the powder modifier of EXAMPLE 1 was added to the mortar at the commencement of the mixing cycle.

The bond strength of the mortar was then tested on clay bricks and concrete blocks in accordance with AS 1640 and AS 1475 respectively. In both test methods, bond strength is determined by bending tests carried out on piers tested at the two ends and loaded as specified in the relative Standard.

The bending test is illustrated with reference to AS 1640 in FIG. 1 wherein a pier comprising nine clay bricks 1 bonded together with mortar 2 between the bricks is supported at each end by further bricks 3. The pier is then loaded by carefully stacking bricks 4 on the centre three bricks 1 until the beam breaks.

The modulus of rupture (bond strength) is determined from $\frac{M}{Z}$ (MPa)

where M = central bending moment at failure in newton millimetres (N.mm)

$= 1.23\ W_1L + 1.63\ W_2L$

W_1 = effective mass of the beam in kilograms

$= \left(\frac{n-2}{n-1}\right) W$

where W = actual mass of beam (kg)

n = number of courses in pier

W_2 = mass of load (kg)

L = clear span (mm)

Z = section modulus of the pier (mm^3).

Bond strength may also be tested as bond in shear as provided by the relevant Standards. Comparative results are shown in the Table in FIG. 2 from which it can be seen that for concrete blocks in particular, bond

strengths of a mortar modified [illegible] invention may be improved by [illegible] compared with unmodified mortars.

In use the laying of [illegible] blocks, the modified mortar was [illegible] workability for periods substantially [illegible] unmodified mortars [illegible] the masonry blocks are bedded [illegible] that despite the extended workability [illegible] bedding, there is an early stiffening [illegible] such that successive courses of [illegible] at normal or higher than normal rates.

Even under extremely [illegible] high ambient temperatures and [illegible] with a high initial rate of absorption the workability and [illegible] strength of the mortar remains substantially unaffected.

While the mechanism of the present invention is not clearly understood, mortars modified in accordance with the present invention have extended workability, [illegible] they exhibit rapid hydration characteristics when a masonry block is bedded. This anomalous behaviour is not only beneficial in the physical act of laying of clay bricks, concrete blocks and the like but is also accompanied by substantially improved physical, chemical and mechanical properties of the mortar itself.

The hydrated mortar has excellent compressive strength, reduced porosity and exhibits substantially no efflorescence. In short, mortars modified in accordance with the present invention exhibit none of the problems usually associated with mortars modified with the prior art modifiers or modifier combinations.

It is anticipated that the present invention would be equally applicable to concrete for manufacture of [illegible] concrete products with similar resultant advantages. In particular the modifier according to the invention may be

used in pumping of concrete to maintain workability and to prevent water separation. Addition of the modifier to cementitious renders or plasters assists workability and maintains a "wet edge" for subsequent edge joints.

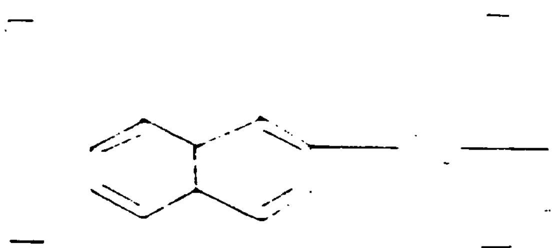
It will be readily apparent to a skilled addressee that many variations or modifications may be made to the present invention without departing from the spirit and scope thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A modifier for cementitious mortars and the like comprising -

[illegible] parts by weight of hydroxy propyl methyl cellulose,

[illegible] parts by weight of a sodium salt of a naphthalene formaldehyde sulphonate of the general formula



wherein n is from [illegible]

and a substantially chlorine free non efflorescing cement accelerator.

2. A modifier as claimed in claim 1 wherein said hydroxy propyl methyl cellulose has a molecular weight of from [illegible],000 - 120,000

3. A modifier as claimed in claim 1 or claim 2 wherein said modifier comprises a dry powder readily soluble in water at ambient temperatures

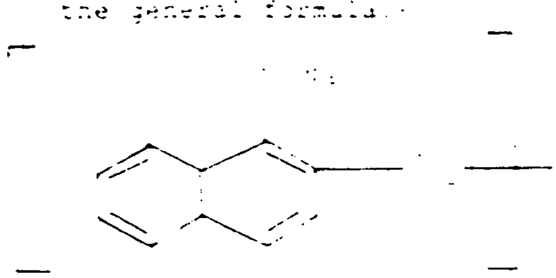
4. A modifier as claimed in any preceding claim wherein said accelerator comprises calcium formate

5. A modifier for cementitious mortars and the like comprising:-

(i) [illegible] parts by weight of hydroxy propyl-

methyl cellulose having a molecular weight in the range 85,000 - 95,000

(ii) 26-74 parts by weight of a sodium salt of naphthalene formaldehyde sulphonate having the general formula:-



wherein n is from 1-10,

(iii) 6-26 parts by weight of calcium formate.

6. A modified cement mortar having the composition - 1 part by volume of portland cement, 1-6 parts by volume of sand, and 0.001-0.010 parts by volume of a modifier as defined in any one of claims 1-5.

7. A method of modifying a cementitious mortar or the like comprising mixing together the dry mortar ingredients with 0.001-0.010 parts by weight of a dry powdered modifier according to any one of claims 1-5 and subsequently adding water to a desired consistency.

8. A modifier for cementitious mortars and the like substantially as hereinbefore described with reference to the examples.

DATED this Second Day of March, 1988

A.V. SYNTEC PTY. LTD.
By its Patent Attorneys
G. R. CULLEN & CO.

FIG. 1

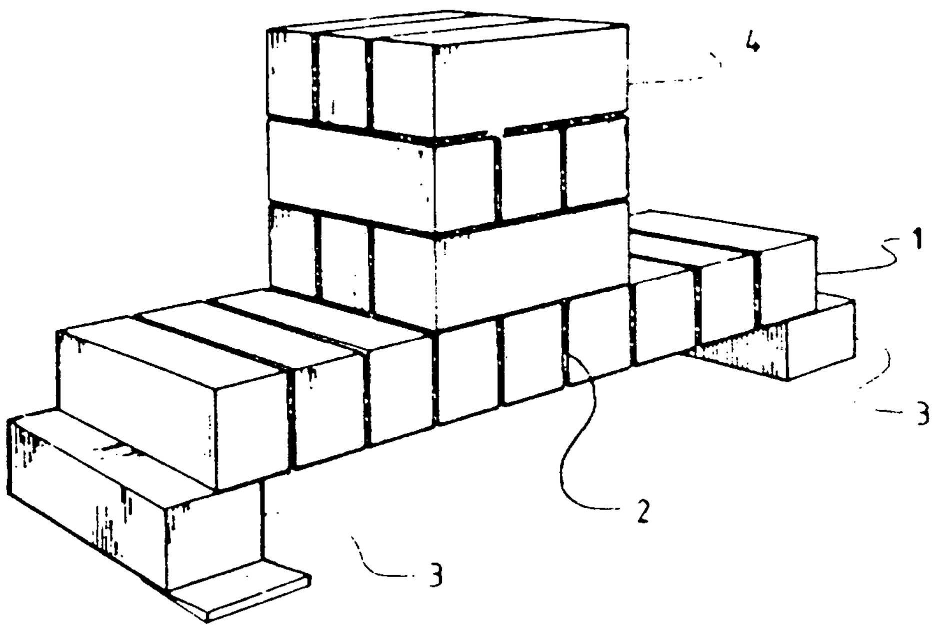
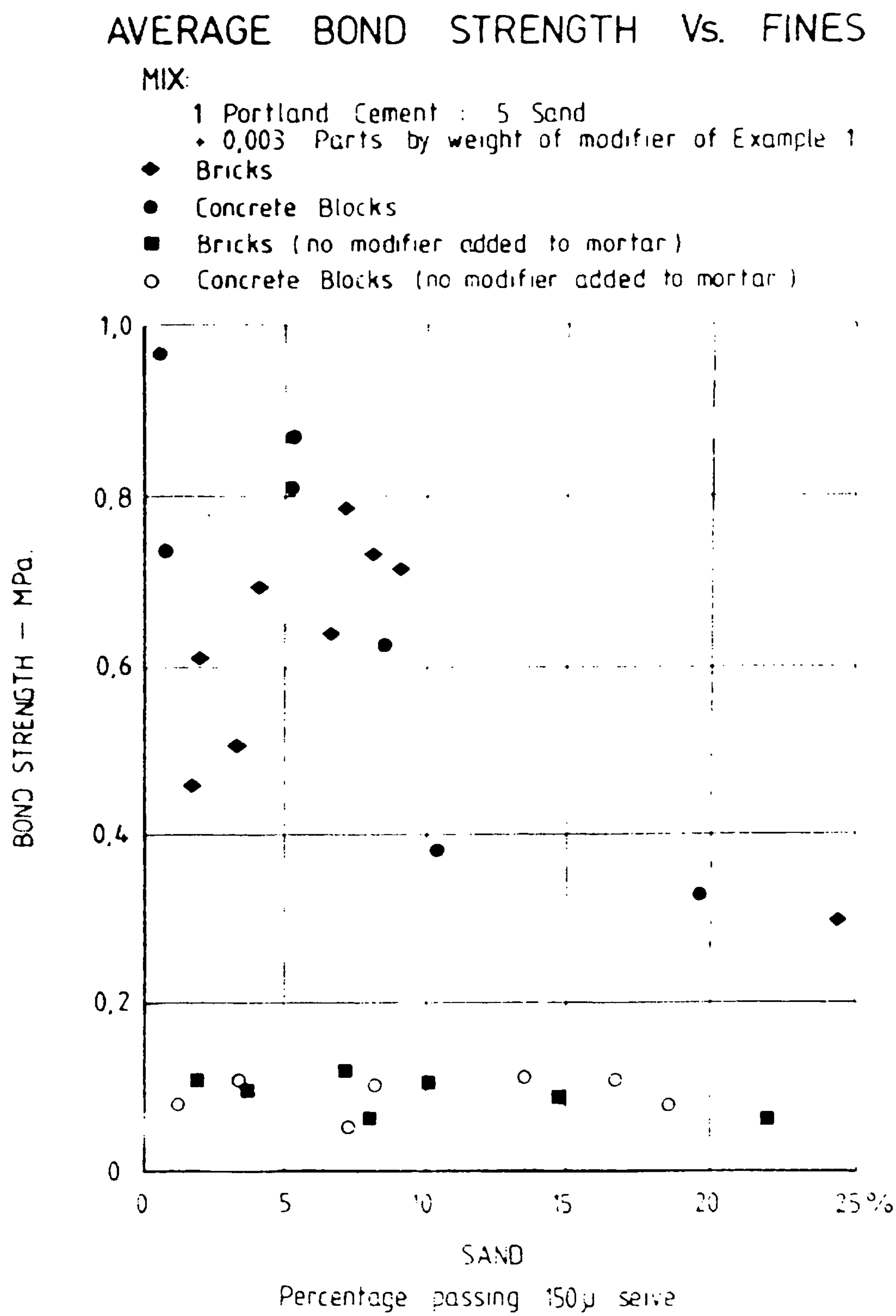


FIG. 2


AVERAGE BOND STRENGTH Vs. FINES
MIX:
1 Portland Cement : 5 Sand
+ 0,003 Parts by weight of modifier of Example 1
Bricks
Concrete Blocks
Bricks (no modifier added to mortar)
Concrete Blocks (no modifier added to mortar)
BOND STRENGTH — MPa.
1,0
0,8
0,6
0,4
0,2
0
0
5
10
15
20
25 %
SAND
Percentage passing 150μ seive